Nuclear Magnetic Resonance Spectroscopy

Features:

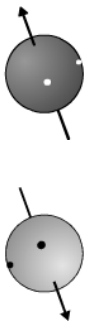
- Used to identify products of reactions
- Also gives information about chemical environment, connectivity and bonding of nuclei

Requirements:

- Pure or mostly pure sample of material (not useful for analyzing mixtures)
- > 1 mg material

Nuclear Magnetic Resonance Spectroscopy Depends on Nuclear Spin

Nucleus	Spins	Isotope Abundance
^{1}H	±½	99.9%
^{12}C	0	98.9%
^{13}C	±½	1.1%
^{19}F	±½	100%
^{31}P	±½	100%



spin

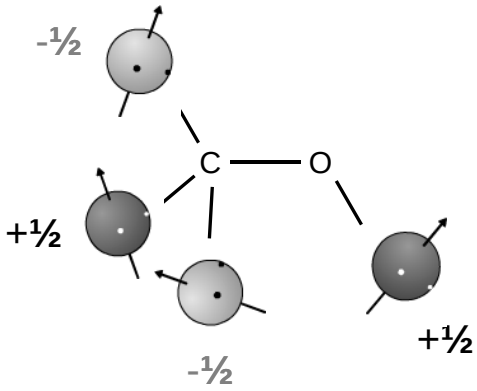
+½

-½

We'll be talking about spectroscopy of ^{1}H (and later ^{13}C).

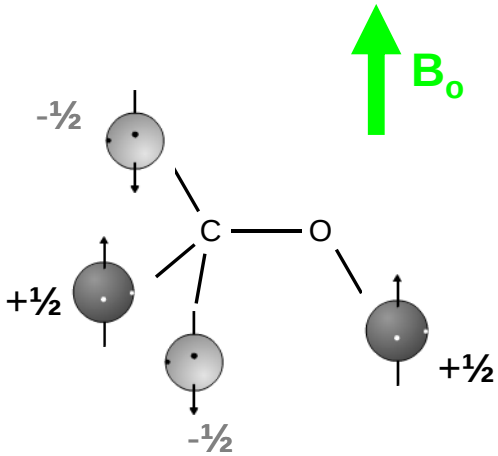
Each ^{1}H Nucleus Has Its Own Spin

We'll consider ^{1}H nuclei in CH_3OH as an example.



In the absence of an applied field, nuclei are randomly oriented.

Nuclear Spins Are Aligned By An Applied Magnetic Field

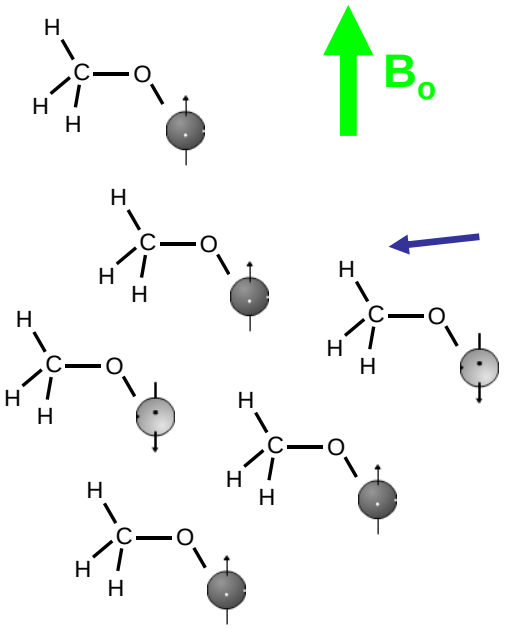


In the absence of an applied field, nuclei are randomly oriented.

In the presence of an applied field $\mathbf{B_o}$, nuclei are oriented by the field.

+ spins align with the field,
- spins align against the field.

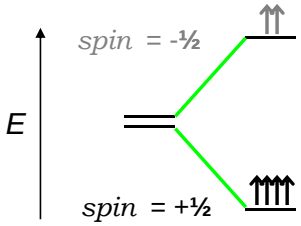
Overall, Applied Field Leads to Bulk Spin Magnetization



Being aligned with field is more stable than against field.

So, more spins align with the field.

Boltzmann population distribution



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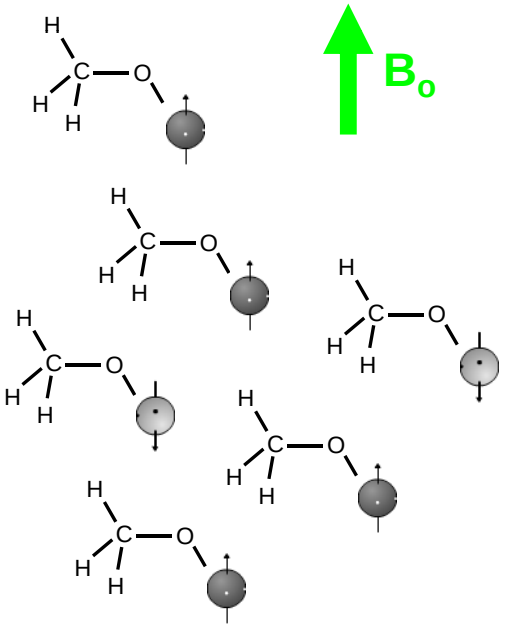


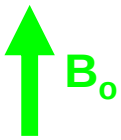
Being aligned with field is more stable than against field.

So, more spins align with the field, and sum of spins also aligns with the field.

= **M**

bulk magnetization

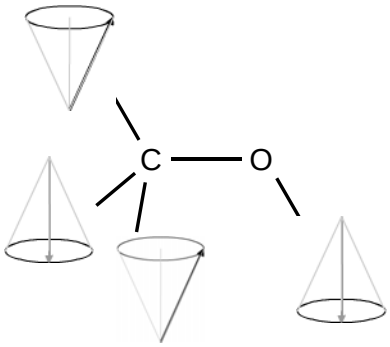
Spins, And Overall Spin, Precess (Wobble) in Applied Magnetic Field



M

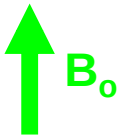
bulk magnetization

Again, using CH_3OH as an example,



All nuclei wobble at a characteristic frequency.

Spins, And Overall Spin, Precess (Wobble) in Applied Magnetic Field



Nuclei precess at the **Larmor frequency.**

$$\nu_o = \frac{\gamma B_o}{2\pi}$$

M

bulk magnetization

B_o	4.73 T	9.46 T	11.75 T
ν_o (^{1}H)	200 MHz	400 MHz	500 MHz
ν_o (^{13}C)	50 MHz	75 MHz	125 MHz

(Precession is fast.)

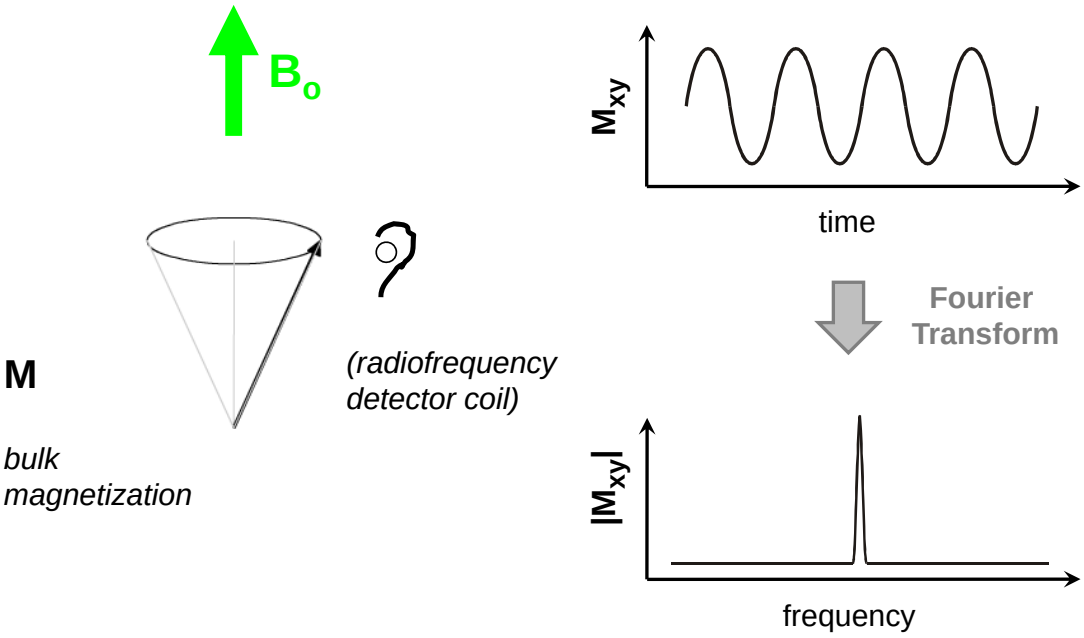
Big Fields Means Big Magnets

Interior of a 4.73 T magnet (on display in NMR Facility, Smith Hall)

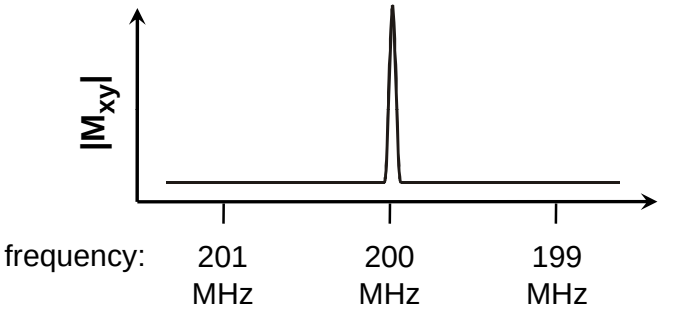
Installation of 16.45 T magnet in Hasselmo Hall.

An NMR Facility

An NMR Spectrometer "Listens" to Frequency of Nuclear Precession

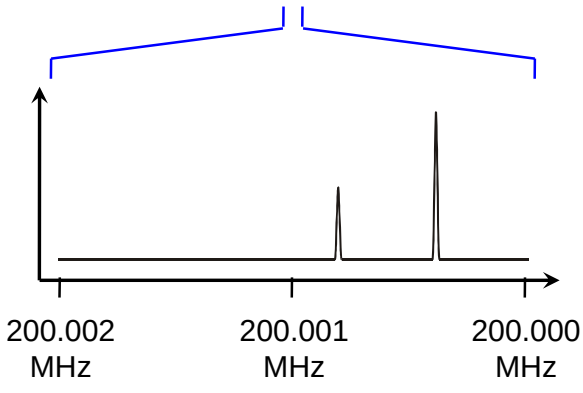


An NMR Spectrum



No surprise: NMR spectrum of CH_3OH shows the presence of ^1H nuclei at Larmor frequency.

but what if we look closer??

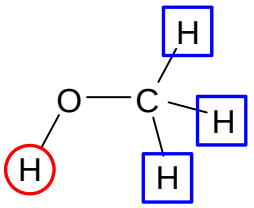


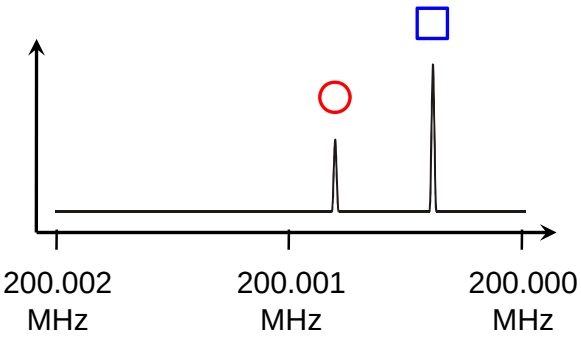
Not all ^1H nuclei wobble at the exact same frequency;

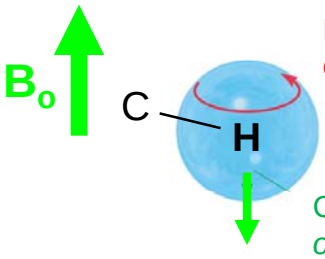
Differences in frequency reflect differences in magnetic environment.

“Shielding” Influences Proton Frequency

NMR spectrum of CH_3OH:



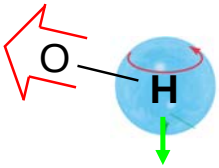




Magnetic field induces circulation of e^- cloud.

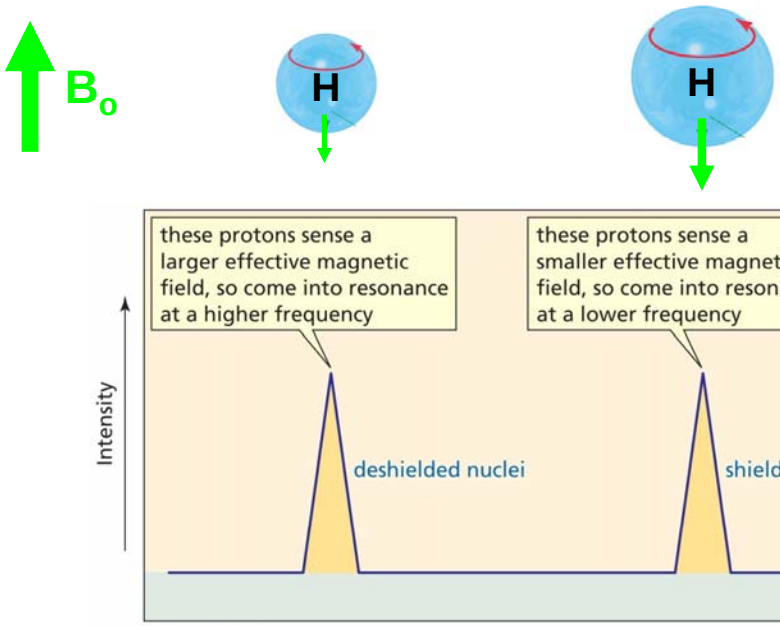
Circulation generates an *opposing* magnetic field.

So, magnetic field and frequency are *lower* than one might expect.



Electron-withdrawing oxygen means
- Smaller e^- cloud on H
- Less opposing magnetic field
- **Higher frequency**

“Shielding” Influences Proton Frequency



Electron cloud “shields” ^1H nucleus.

“downfield”: Lower magnetic field strength would be required to achieve the same frequency.

← frequency ←

“upfield”: Higher magnetic field strength would be required to counteract shielding electrons and achieve the same frequency.

Chemical Shift:
A Proportional Horizontal Axis

Problem: Differences in frequency depend on spectrometer field strength, vary from instrument to instrument.

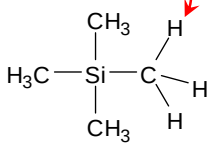
Solution: Define an absolute scale independent of spectrometer frequency, called “chemical shift”.

$$\text{chemical shift, ppm } \delta = \frac{\text{shift downfield from TMS (in Hz)}}{\text{spectrometer frequency (in MHz)}}$$

frequency

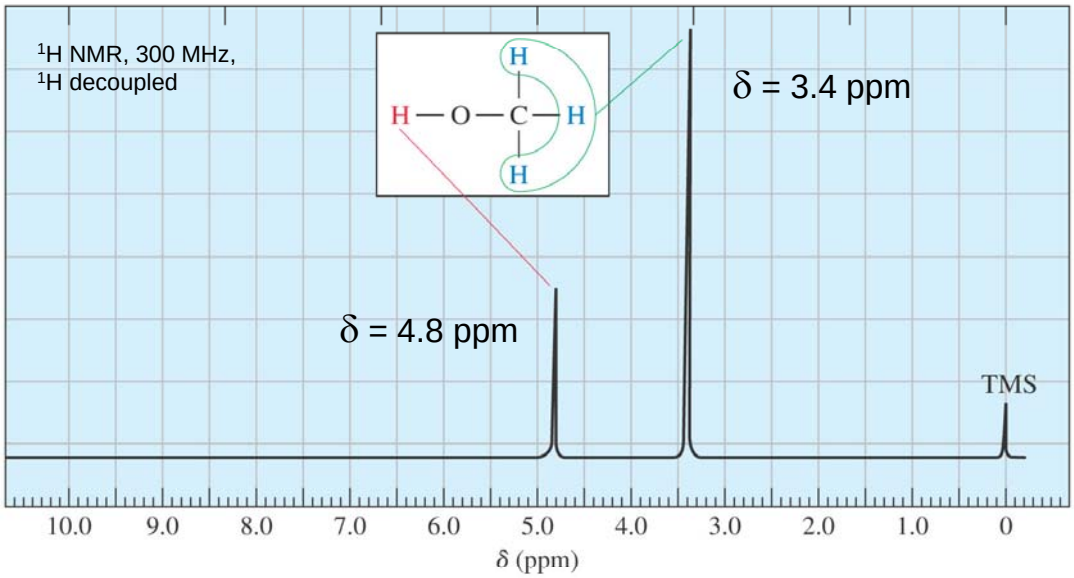
200.002	200.001	200.000	MHz
2000	1000	0	Hz (*diff.*)
10	5	0	ppm

Frequency defined as δ = 0 ppm



tetramethylsilane (TMS)

Chemical Shift:
A Proportional Horizontal Axis



CH_3OH protons have these chemical shifts (ppm values), regardless of instrument they are measured on.

Different Types of Protons Have Characteristic Chemical Shifts

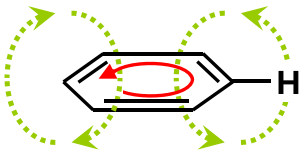
TABLE 13-3 Typical Values of Chemical Shifts

Type of Proton	Approximate δ	Type of Proton	Approximate δ
alkane ($-CH_3$)	0.9	$>C=C<_{CH_3}$	1.7
alkane ($-CH_2-$)	1.3	Ph—H	7.2
alkane ($-CH<$)	1.4	Ph—CH_3	2.3
$-C(=O)-CH_3$	2.1	R—CHO	9–10
$-C\equiv C-H$	2.5	R—COOH	10–12
R—CH_2—X (X = halogen, O)	3–4	R—OH	variable, about 2–5
		Ar—OH	variable, about 4–7
$>C=C<_{H}$	5–6	R—NH_2	variable, about 1.5–4

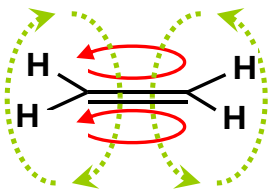
A better resource: http://www.chem.wisc.edu/areas/reich/Handouts/nmr-h/hdata.htm

Chemical Shift: Multiple Bonds and Induced Current

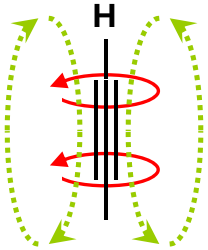
In presence of applied field B_0 ,



"Ring current" *reinforces* applied B_0 field; **deshields** aromatic protons (δ = 6.5-8.5 ppm).



Induced current is less effective in olefins, still **deshields**, but less (δ = 4-6 ppm).



Acetylene protons are **shielded** (δ = 1.5-3 ppm).